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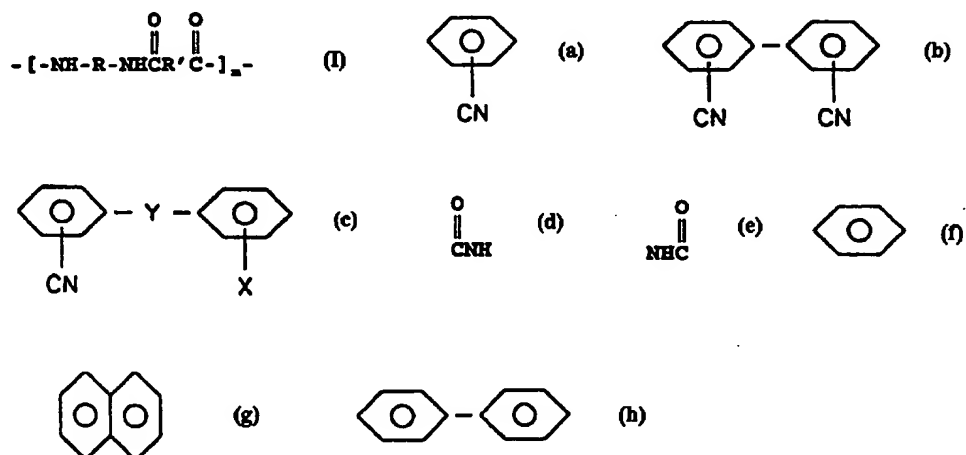
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(54) Title: AROMATIC POLYAMIDE, OPTICAL ANISOTROPIC DOPE AND ARTICLES AND PREPARATION FOR THE SAME



(57) Abstract

Described in this invention is an aromatic polyamide of structural formula (I) for preparing an optical anisotropic dope under the conditions of less activity than sulfuric acid, less environmental contamination and easiness in process control, wherein R represents an aromatic group such as (a), (b) or (c) having a nitrile group substituted on the aromatic nucleus of which amount is 25 to 100 mol% of the total aromatic group; where X represents H, Cl, Br, I, NO₂, or an alkoxy group having 1 to 4 carbon atoms, n represents an integer between 10 and 100,000, y represents (d) or (e), and R' represents (f), (g) or (h).

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AROMATIC POLYAMIDE, OPTICAL ANISOTROPIC DOPE AND
ARTICLES AND PREPARATION FOR THE SAME

BACK GROUND OF THE INVENTION

5

Field of the Invention

10 The present invention relates to an aromatic
polyamide, in particular to a novel aromatic polyamide
forming an optical anisotropic dope which is easily
dissolved in a polar organic solvent and preparing
thereof, an optical anisotropic aromatic polyamide dope
and preparing thereof and a high modulus aromatic
polyamide fibroid article prepared from the optical
15 anisotropic aromatic polyamide dope.

Description of the Related Art

20 In general, aromatic polyamide films and articles
thereof are used valuably in composite materials of air
craft and automobile industry, building materials and
leisure and sports goods because they have a high
strength, high modulus, heat resistance, abrasion
resistance and insulating property.

25 Due to such utilities, there have been developed
various processes for producing aromatic polyamide
fibers and preparations for the articles. In case of an
optical anisotropic aromatic polyamide dope, high
strength and high modulus fiber can be prepared without
30 drawing process because polymer chains are already
arranged along the axis of the fiber during extrusion
spinning from the nozzle, researches for preparing
thereof have been actively performed.

35 For example, Du-pont Inc. discloses an industrial
process wherein polybenzamide and polyparaphenylene
terephthalamide are dissolved by heating with 100 %

sulfuric acid to prepare an optical anisotropic aromatic polyamide dope and high strength and high modulus aromatic polyamide fibers are prepared by extrusion spinning (U.S. patents Nos. 3,671,542 and 3,673,143).

5 U.S. patent No. 4,018,735 discloses a process wherein an aromatic polyamide prepared by incorporating 5 to 35 mole % of hetero ring unit of benzoxazol or imidazol is dissolved with sulfuric acid to produce an anisotropic aromatic dope.

10 Processes disclosed in the above papers include the use of 100 % of sulfuric acid for heating and dissolving an aromatic polyamide to prepare an optical anisotropic dope of an aromatic polyamide, however the use of sulfuric acid leads to the decrease in the physical
15 property by deteriorating the degree of polymerization during dissolving, environmental contamination and difficulty in process control.

SUMMARY OF THE INVENTION

20 The first object of the present invention is to provide a novel aromatic polyamide which can be used to produce an optical anisotropic aromatic polyamide dope under easy conditions.

25 The second object of the present invention is to provide an optical anisotropic aromatic polyamide dope which contains the above aromatic polyamide and does not contain sulfuric acid and a process for preparing the same.

30 The third object of the present invention is to provide a high strength and high modulus aromatic polyamide fiber of which component is mainly the above novel aromatic polyamide.

35 BRIEF DESCRIPTION OF THE DRAWINGS

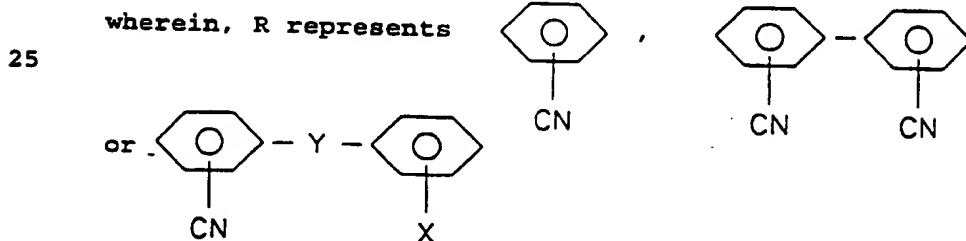
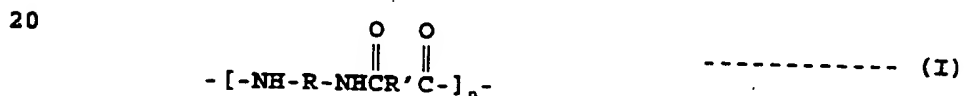
Fig. 1 is a phase transition diagram of a polymer according to the concentration of an inorganic salt and the polymer in a polar solvent;

Fig. 2 is a phase transition diagram of a polymer according to the degree of polymerization of the polymer and the concentration of a polymer in a polar solvent; and

Fig. 3 is a phase transition diagram of a polymer according to the concentration of the polymer and the viscosity of the polymer dope.

DETAILED DESCRIPTION OF THE INVENTION

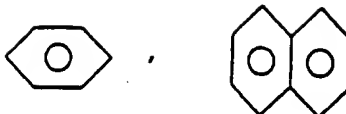
In order to achieve the first object, the present invention provides an aromatic polyamide represented by the following structural formula (I)



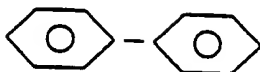
where X represents H, Cl, Br, I, NO₂, or an alkoxy group having 1 to 4 carbon atoms, n represents an integer between 10 and

100,000, and y represents $\overset{\text{O}}{\parallel}\text{CNH}$ or $\overset{\text{O}}{\parallel}\text{NHC}$

R' represents



5 or



Particularly, the amount of the aromatic diamine, which forms a repeating unit of the above structural formula (I), having a nitrile group substituted on the aromatic nucleus is at least 25 mol %, preferably 25 to 100 mol % in the total aromatic diamine.

The aromatic polyamide of the above structural formula (I) is obtained by polycondensation with an aromatic diacid halide under the condition that the amount of the aromatic diamine having a nitrile group substituted on the aromatic nucleus is at least 25 mol %, preferably 25 to 100 mol % in the total aromatic diamine.

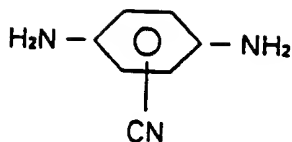
Both an aromatic diamine having a nitrile group substituted on the aromatic nucleus or that not having a nitrile group can be used for the aromatic diamine of the present invention, however, it is a characteristic of the present invention that the amount of the aromatic diamine having a nitrile group substituted on the aromatic nucleus is at least 25 mol %, preferably 25 to 100 mol % in the total aromatic diamine. Typical examples are as follows, however, the present invention is not limitatively defined by the followings as shown in the general structural formula (I).

diaminobenzanilide

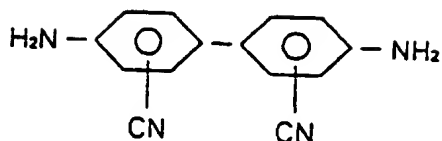
benzidine

phenylenediamine

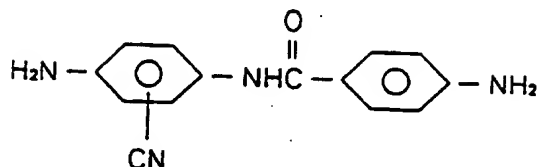
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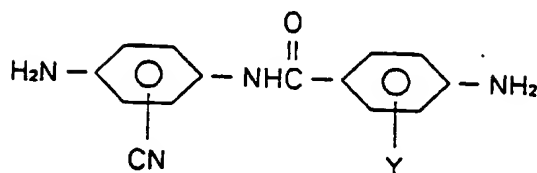
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(wherein, Y represents Cl, Br, I, NO₂ or an alkyl or alkoxy group having 1 to 4 carbon atoms.)

25

Typical examples of an aromatic diacid halide which can be used in the present invention include terephthalic chloride, isophthalic chloride, naphthalic chloride and diphenyl chloride which may be unsubstituted or substituted with Cl, Br, I, NO₂, or an alkyl or alkoxy group having 1 to 4 carbon atoms.

30

The aromatic polyamide represented by the above formula (I) is a novel high molecular weight aromatic polyamide having an intrinsic viscosity of 2.0 or higher, preferably 2 to 10, which is soluble in a polar organic solvent, and the amount of diamine component having a nitrile group substituted on the aromatic nucleus is at least 25 mol %, preferably 25 to 100 mol % in the total

35

diamine component.

The intrinsic viscosity can be calculated from the following formula by the measurement using an Ubbelohde viscometer and extrapolation of 5 selected dilute concentrations (in 98 % sulfuric acid at 30°C):

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$$

$$\eta_{sp} = \eta_r - 1$$

$$\eta_r = \frac{t}{t_0}$$

where t is the time period taken for the solution to pass the viscometer,

t_0 is the time period taken for the solvent to pass the viscosimeter, and

C is the concentration of the solution.

The aromatic polyamide of the present invention can be confirmed by the absorption band of a nitrile group in the infrared spectrum at 2230 cm^{-1} .

The process for producing an aromatic polyamide of the structural formula (I) to achieve the second object of the present invention by forming an optical anisotropic aromatic polyamide polymerization dope of which the polymerization solution shows silver-white brightness during polymerization comprises the following steps of:

preparing a solvent for polymerization from an amide type organic solvent, an urea type organic solvent or a mixture thereof;

adding and dissolving an aromatic diamine having a nitrile group substituted on the aromatic nucleus in the solvent for polymerization;

adding pyridine as a polycondensation catalyst in the resulting solution;

adding the aromatic diacid halide in the solution with vigorous stirring at 0 to 50°C; and

5 continuing stirring for 1 to 360 minutes at the temperature to obtain a high viscous polymer solution which shows silver-white brightness during stirring.

In addition, the process for producing an aromatic polyamide of the structural formula (I) to achieve the
10 second object of the present invention by forming an optical anisotropic aromatic polyamide polymerization dope of which the polymerization solution shows silver-white brightness during polymerization comprises the following steps of:

15 preparing a solvent for polymerization from an amide type organic solvent, an urea type organic solvent or a mixture thereof;

adding and dissolving an aromatic diamine having a nitrile group substituted on the aromatic nucleus in the
20 solvent for polymerization;

adding the aromatic diacid halide in the solution with vigorous stirring at 0 to 50°C;

keeping the gel type polymer obtained in the above step for 0 to 24 hours;

25 adding and dissolving an inorganic alkali compound selected from the group consisting of an alkali metal such as Li_2CO_3 , CaCO_3 , LiH , CaH_2 , LiOH , Ca(OH)_2 , Li_2O or CaO , carbonate of alkali earth metal, hydride, hydroxide or oxide with stirring for 1 hour to a few day; and

30 obtaining a highly viscous polymer solution which shows silver-white brightness during stirring.

The above high viscosity polymer solution is an optical anisotropic polyamide dope showing various colors through the polarized microscope, and it is
35 easily treated to articles such as polyamide fibers having high strength and high modulus, films and pulps

by spinning through a nozzle into a coagulating bath. Additionally, not containing sulfuric acid in the optical anisotropic polyamide dopes of the present invention leads to no deteriorating of degree of polymerization of polyamide and easiness in process control.

As an organic solvent of the present invention, all organic solvents of amide or urea type can be used but it is preferable to use N-methyl-2-pyrrolidone (NMP), N,N-dimethyl acetamide (DMAC), hexamethyl phosphoamide (HMPA), N,N,N',N'-tetramethyl urea (TMU), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) or a mixture thereof.

An inorganic salt may be further added to a solvent for polymerization used in the present invention in order to increase the solubility. Typical examples of the inorganic salt include an alkali metal halide or an alkali earth metal halide such as CaCl_2 , LiCl , NaCl , KCl , LiBr and KBr .

An inorganic salt can be added in the solvent for polymerization by itself or as a mixture of 2 or more. The added amount of the inorganic salt is desirably 12 % by weight or lower based upon the weight of solvent for polymerization. The amount higher than 12 % by weight is economically disadvantageous because the desired effects of the present invention cannot be expected.

A by-product (HCl) is produced by the reaction between an aromatic diamine and an aromatic diacid chloride in the third step of the latter process for producing an aromatic polyamide of the structural formula (I). To remove it from the polymerization process, an inorganic alkali compound selected from the group consisting of an alkali metal such as Li , CO_2 , CaCO_3 , LiH , CaH_2 , LiOH , Ca(OH)_2 , Li_2O or CaO , carbonate of alkali earth metal, hydride, hydroxide or oxide is added. An

inorganic alkali compound or a mixture comprising 2 or more of it can be added and its added amount is desirably 10 to 200 mol % of the required equivalent to neutralize the HCl.

5 In addition, the second object of obtaining silver white optical anisotropic dope of the present invention can be also achieved by dissolving an aromatic polyamide of the structural formula (I) of which amount is 7 % by weight or more in a polar organic solvent having 1 % by
10 weight or more of an inorganic salt at 0 to 100°C, preferably 20 to 70°C.

As a polar organic solvent, all organic solvents of amide or urea type can be used but it is preferable to use N-methyl-2-pyrrolidone (NMP), N,N-dimethyl acetamide
15 (DMAc), hexamethyl phosphoamide (HMPA), N,N,N',N'-tetramethyl urea (TMU), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) or a mixture thereof.

Typical examples of the inorganic salt of the present invention include an alkali metal halide or an
20 alkali earth metal halide such as CaCl₂, LiCl, NaCl, KCl, LiBr and KBr.

An inorganic salt can be added by itself or as a mixture of 2 or more. It is necessary that the added amount of the inorganic salt is at least 1 % by weight,
25 desirably 1 to 10 % by weight. An amount lower than 1 % by weight is not desirable to produce an optical anisotropic dope because the solubility of the polyamide of the structural formula (I) is decreased in the organic polar solution. An amount higher than 10 % by
30 weight is economically disadvantageous because the solubility of polyamide is not increased by increasing the amount of the inorganic salt.

The concentration of the polyamide in an organic polar solution for preparing an optical anisotropic dope
35 can be changed according to the degree of polymerization of the polyamide, the viscosity of the dope or the

concentration of the inorganic salt in the polar organic solvent, however, it is desirable to have at least 7 % by weight, preferably 7 to 23 % by weight of the polyamide. For a concentration of lower than 7 % by weight, the optical property of the dope shows isotropy because of having a low amount of the polymer. For a concentration of higher than 23 % by weight, the effects of the present invention cannot be expected because the dope is present in the state of a solid (Fig. 1).

Additionally, it is desirable that the degree of polymerization of the polyamide represented by the structural formula (I) is at least 2 or more of the limiting viscosity for preparing an optical anisotropic polyamide dope of the present invention.

With the degree of polymerization of the polyamide lower than 2 of intrinsic viscosity, an optical anisotropic dope of the present invention can not be obtained though the concentration of the polyamide is increased in an organic polar solvent (Fig. 2).

Further, the viscosity of the dope with the content of the polymer in it also has heavy effects on the optical property of the dope.

With the viscosity of the dope higher than 1000 poise and the content of the polymer 10 to 20 % by weight, an optical anisotropic dope can be obtained (Fig. 3).

Fig. 1 is an isotropic and anisotropic phase transition diagram according to the concentration of the polymer and DMAc-LiCl when the aromatic polyamide of structural formula (I) of the present invention is dissolved in the DMAc-LiCl solution.

As shown in Fig. 1, when the content of the inorganic salt (LiCl) is lower than 1 % by weight in the polar organic solvent (DMAc), the optical isotropy is shown in the dope because the solubility of the polyamide is decreased or the dope is present in the

state of a solid. When the concentration of the polymer is 7 to 23 % by weight in the polar organic solvent, the optical anisotropy is shown in the dope.

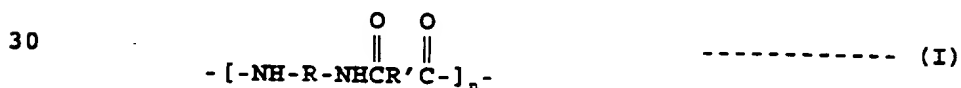
Fig. 2 is an isotropic and anisotropic phase transition diagram according to the intrinsic viscosity of the degree of polymerization of the aromatic polyamide represented by the structural formula (I) of the present invention and the concentration of LiCl is 4 % by weight of the DMAc.

As shown in Fig. 2, even with the concentration of the polymer higher than 7 % by weight, the concentration at which the dope shows the optical anisotropic, if the degree of polymerization is lower than 2 of intrinsic viscosity, the optical anisotropy is not shown in the dope.

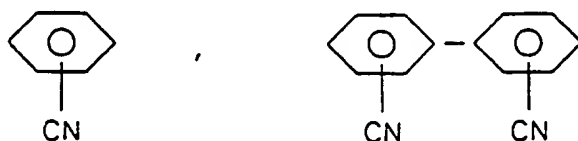
Fig. 3 is a diagram in which the concentration (the concentration of LiCl is 4 % by weight of the DMAc) of the aromatic polyamide represented by the structural formula (I) and the viscosity of the dope are shown.

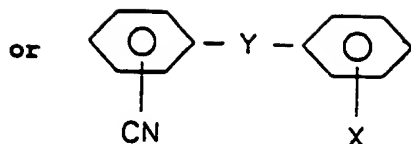
As shown in Fig. 3, the optical anisotropy is shown at certain concentration (from 10 to 20 % by weight), wherein the viscosity of the dope is lower than that of the dope showing isotropy.

In order to achieve the third object, the present invention provides the aromatic polyamide fiber, pulp or articles of film which forms repeating unit represented by the following structural formula (I):



wherein, R represents an aromatic diamine such as





5 wherein an amount of the aromatic diamine having a nitrile group substituted on the aromatic nucleus is at least 25 mol % of the total aromatic diamine;
 and X represents H, Cl, Br, I, NO₂, or an alkoxy group having 1 to 4 carbon atoms, n represents an integer
 10 between 10 and

100,000, y represents CNH or NEC , and R' represents



The aromatic polyamide fiber which forms the repeating unit represented by the structural formula (I) has a high strength and high modulus property (the
 20 tensile strength is 10 g/d or more and the tensile modulus is 450 g/d).

The aromatic polyamide fiber, pulp or article of film of the present invention is produced by spinning, coagulating, washing and drying as follows:

25 an optical anisotropic polyamide dope having an aromatic polyamide of the above structural formula (I) which is obtained by polycondensation with an aromatic diacid halide monomer under the condition that an amount of the aromatic diamine having a nitrile group
 30 substituted on the aromatic nucleus is at least 25 mol %, preferably 25 to 100 mol % in the total aromatic diamine in the solvent for polymerization adding the inorganic salt such as an alkali metal halide or an alkali earth metal halide to the polar organic solvent
 35 including an amide type organic solvent, an urea type

organic solvent or a mixture thereof with pyridine catalyst at 0 to 50°C;

an optical anisotropic polyamide dope having an aromatic polyamide of the above structural formula (I) obtained by adding an inorganic salt such as an alkali metal halide or an alkali earth metal halide to the gel type polymer which is obtained by polycondensation with an aromatic diacid halide monomer under the condition that the amount of the aromatic diamine having a nitrile group substituted on the aromatic nucleus is at least 25 mol % in the total aromatic diamine with the polar organic solvent including an amide type organic solvent, an urea type organic solvent or a mixture thereof at 0 to 50°C; or

an optical anisotropic polyamide dope which is obtained by dissolving the aromatic polyamide represented by the structural formula (I) in the polar organic solvent including the inorganic salt such as an alkali metal halide or an alkali earth metal halide according to the general production process of polyamide fibers, pulps or films.

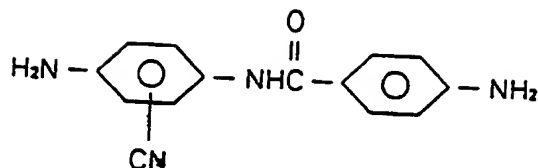
The preferred examples will be described hereinafter to illustrate the present invention, but not limiting to it.

EXAMPLE 1

Preparation of an aromatic diamine monomer (4,4'-diamino-6-cyanobenzanilide) having a nitrile group substituted on the aromatic nucleus

a) Preparation of 4,4'-dinitro-6-cyanobenzanilide

5



100 g (0.613 mol) of 5-nitro-anthranitrile was added to be dissolved in 640 ml of dimethylacetamide (DMAC) which was stirred under nitrogen stream. Then, 49.6 ml (0.613 mol) of pyridine was added to the solution and it was cooled to 5 to 10°C in an ice bath. After cooling, 116.0 g (0.613 mol) of 4-nitrobenzoyl chloride in a powder form was added to the solution with vigorous stirring. The color of the solution was bright, violet and transparent in the initial stage. Then, it was changed to orange and translucent after an hour, and finally, to yellow and transparent after 4 days with stirring at ambient temperature. Yellow and transparent solution was obtained by filtering the above solution (if crystals are produced, additional DMAC is added to dissolve them). Reddish brown high viscous solution was obtained by distilling the above solution. Then, the solution was added to distilled water to solidify with stirring and filtered, washed with water and then washed with boiling ethanol and acetone twice, respectively. The solution was filtered and then dried in a vacuum oven at 60°C to obtain 145 g of the raw material (yield was 76 %).

b) Preparation of 4,4'-diamino-6-cyanobenzanilide (DACYB)

(METHOD 1)

900 ml of ethanol was charged into a 2 liter 4-bulb round flask under nitrogen stream, and 100 ml of

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cyclohexene, 5 g of palladium/carbon (5 wt.%) and 20 g (0.064 mol) of 4,4'-dinitro-6-cyanobenzanilide were added with stirring. Then, the solution was refluxed using an oil bath at 85 to 90°C. The dispersed solution showed yellow-earthly color in the initial stage and lost the yellow color as the time went by and then showed completely black color after 3 to 4 hours later with producing colorless crystals. 20 g of 4,4'-diamino-6-cyanobenzanilide was additionally added respectively 3 times, but even after 6 hours later, the yellow color was not disappeared after the second addition. In the third addition, the yellow color was disappeared by additional adding of 50 ml of cyclohexene and 1 g of palladium/carbon (5 % by weight) with stirring over night. After the reaction, the solution was filtered and treated with an activated carbon to recrystallize and then recrystallized again in a mixture solvent (acetone : ethanol = 1 : 1) by soxlet. After the reaction, the filtered solid was washed with acetone twice. The solution was filtered, treated with an activated carbon to recrystallize and dissolved in the mixture solvent (acetone : ethanol = 1 : 1) to separate with the palladium/carbon (5 % by weight). The solid was recrystallized by soxlet and the liquid was treated with the activated carbon, filtered, and separated by repeated recrystallization by soxlet. The separated solid was dried in a vacuum oven to obtain 60.5 g of the raw material (yield was 83.7 %). The melting point of the obtained raw material was 250 to 251°C.

(METHOD 2)

350 ml of oleum (30 % by weight) was cooled down below 0°C using an ice bath, 99.6 g (0.368 mol) of 4,4'-diamino-6-carbamoyl benzanilide in a powder form was added below 5°C with stirring. The stirring was

continued to the next day, and the solution was neutralized by adding 1100 ml of NH_4OH (28 % by weight) already cooled down to -5 to 0°C . The solution was sufficiently washed to remove salt by filtering and washed with a small amount of warm ethanol and then dried in a vacuum oven at 80°C . The dried reactant which was mixed with by-products was extracted by soxlet and treated with the activated carbon and then ethanol was added to recrystallize in the mixture solvent (acetone : ethanol = 1 : 1). The light yellow-scalelike crystal was filtered and dried in a vacuum oven at 80°C . The light yellow-scalelike crystal was extracted again by soxlet with acetone and treated with the activated carbon. And then the white-scalelike crystal obtained by recrystallizing in the mixture solvent (acetone : ethanol = 1 : 1) was dried in a vacuum oven at 80°C (40 g of the raw material was obtained and the boiling point thereof was 250 to 251°C).

20

EXAMPLE 2

Preparation of an optical anisotropic aromatic polyamide dope

65 ml of dimethylacetamide (DMAc) was charged into a 250 ml reactor under nitrogen stream, and 1.6 g of LiCl was added and completely dissolved to prepare a solvent for polymerization. 4 g of 4,4'-diamino-6-cyanobenzanilide (DACYB) was added and dissolved completely in the solution. 12.6 ml of pyridine was added and then 3.22 g of terephthaloyl chloride (TPC) was added at once at 10 to 15°C with vigorous stirring. The viscosity of the polymerization solution was increased immediately and the solution become a viscous silver white optical anisotropic dope after a few minutes. The anisotropic dope was examined by a

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polarized microscope. The intrinsic viscosity of the obtained aromatic polyamide was 5.0 (examined in the 30°C, 97 % by weight of sulfuric acid).

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EXAMPLES 3 to 9

Preparation of an optical anisotropic aromatic polyamide dope

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Optical anisotropic dopes were prepared by the same method as EXAMPLE 2 except the amounts of the monomer and the additive. they are listed in the following Table 1.

15

Table 1

| | Components | | | | | | Comp. & Prop. of dope dur. polymeriza. | | Prop. of Pol. Int. Vis. |
|----|------------|-----------|----------------------|----------------|-----------|---------------------|--|------------|-------------------------|
| | TPC (g) | DACYB (g) | LiCl(g)(g/100ml DMAC | pyri-dine (ml) | DMAC (ml) | Conc. of mon. (wt%) | Conc. of pol. (wt%) | Opt. Prop. | |
| 20 | EX.3 | 5.63 | 7 | 1.6 (2.56) | 7 | 65 | 15.4 | 12.9 | ANISO 3.8 |
| | EX.4 | 6.68 | 8.3 | 1.54 (2.56) | 8.7 | 60 | 18.4 | 15.5 | ANISO 4.7 |
| | EX.5 | 9.30 | 11.6 | 2.03 (2.56) | 7.4 | 79.2 | 20.0 | 16.8 | ANISO 8.2 |
| | EX.6 | 6.42 | 7.97 | 1.6 (3.2) | 8.4 | 50 | 20.3 | 17.0 | ANISO 5.9 |
| | EX.7 | 6.43 | 7.98 | 1.7 (3.4) | 8.4 | 50 | 20.3 | 17.0 | ANISO 5.9 |
| 25 | EX.8 | 6.44 | 8 | 1.75 (3.5) | 8.4 | 50 | 20.3 | 17.0 | ANISO 4.0 |
| | EX.9 | 6.48 | 8.05 | 1.9 (3.8) | 8.5 | 50 | 20.3 | 17.0 | ANISO 5.5 |

EXAMPLE 10

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Preparation of an aromatic polyamide filament

The optical anisotropic aromatic polyamide dope prepared in EXAMPLE 4 was extrusion-spun into 0.5 to 2 cm of an air layer through nozzle and, at the same time, coagulated in the 20 % by weight of dimethyl

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18

acetamide aqueous solution at 5°C and then wound into a roller at a maximum speed. After being sufficiently washed with distilled water, the filament was dried in a drier at 150°C. The dried filament had a fineness of 2 denier, a tensile strength of 16 g/d, an elongation of 4.6 % and a tensile modulus of 440 g/d.

EXAMPLES 11 to 13

Preparation of an aromatic polyamide filament

The mechanical properties of the aromatic polyamide filaments prepared by the same method as EXAMPLE 10 are listed in the following Table 2.

Table 2

| | Used Dope | Fineness (denier) | Tensile Strength (g/d) | Elongation (%) | Tensile Modulus (g/d) |
|------------|-----------|----------------------|------------------------------|-------------------|-----------------------------|
| EXAMPLE 11 | EX.6 | 0.6 | 20 | 4.8 | 510 |
| EXAMPLE 12 | EX.7 | 2.0 | 18 | 6.0 | 400 |
| EXAMPLE 13 | EX.8 | 1.3 | 19 | 5.5 | 370 |

EXAMPLE 14

Preparation of an optical anisotropic aromatic polyamide dope

50 ml of dimethylacetamide (DMAc) was charged into a 250 ml reactor under nitrogen stream, and 5.61 g (0.0258 mol) of 4,4'-diamino-6-cyanobenzanilide (DACYB) was added and dissolved in the solution. Then, the solution was cooled down below 20°C with an ice bath and 5.32 g of terephthaloyl chloride (TPC) was added. The solution become rigid at the moment of adding terephthaloyl chloride. On the next day, the rigid polymer was dissolved slowly with adding 1.91 g (0.0258

mol) of Li_2CO_3 and become a clear silver white anisotropic polymer solution. The polymer solution was slowly stirred for an additional day. The anisotropy of the dope was confirmed by a polarized microscope. The intrinsic viscosity of the obtained aromatic polyamide was 3.8 (examined in the 30°C , 97 % by weight of sulfuric acid).

EXAMPLES 15 and 16

Preparation of an optical anisotropic aromatic polyamide dope

Optical anisotropic dopes were prepared by the same method as EXAMPLE 14 except the amounts of the monomer and the additive. They are listed in the following Table 3.

Table 3

| | Components | | | | | Comp. & Prop. of dope dur. polymeriza. | | Prop. of Pol. | |
|-------|------------|-----------|------------------------|----------------|-----------|--|---------------------|---------------|-----------|
| | TPC (g) | DACYB (g) | LiCl(g) (g/100ml DMAC) | pyri-dine (ml) | DMAC (ml) | Conc. of mon. (wt%) | Conc. of pol. (wt%) | Opt. Prop. | Int. Vis. |
| EX.15 | 5.54 | 6.79 | 0 | 1.99 | 50 | 20.0 | 17.2 | ANISO | 4.1 |
| EX.16 | 5.32 | 6.51 | 0.08 | 1.91 | 50 | 20.0 | 16.8 | ANISO | 5.2 |

EXAMPLE 17

Preparation of an aromatic polyamide filament

The optical anisotropic aromatic polyamide dope prepared in EXAMPLE 16 was extrusion-spun into 0.5 to 2 cm of an air layer through nozzle and, at the same time, coagulated in the 20 % by weight of dimethyl

acetamide aqueous solution at 5°C and then wound into a roller at a maximum speed. After being sufficiently washed with distilled water, the filament was dried in a drier at 150°C. The dried filament had a fineness of 1.0 denier, a tensile strength of 18.4 g/d, an elongation of 7.5 % and a tensile modulus of 270 g/d.

EXAMPLE 18

10 Preparation of an optical anisotropic aromatic polyamide dope

50 ml of dimethylacetamide (DMAc) was charged into a reactor and dissolved under nitrogen stream, and 5.51 g (0.0204 mol) of 4,4'-diamino-2-cyanobenzanilide (DACYB) and 1.55 g (0.0068 mol) of 4,4'-diaminobenzanilamide (DAB) were added. After the solution was completely dissolved, 7.2 ml of pyridine was added with stirring. The solution was cooled down below 20°C and then 5.52 g of terephthaloyl chloride (TPC) in a powder form was added. The solution became a viscous polymer solution with an optical anisotropy at the moment of adding terephthaloyl chloride. The polymer solution was slowly stirred for an additional day. The anisotropy of the dope was confirmed by a polarized microscope. The limiting viscosity of the obtained copolymerized aromatic polyamide was 6.6.

30

EXAMPLES 19 to 22

35 Preparation of an optical anisotropic aromatic polyamide dope

Optical anisotropic dopes were prepared by the same method as EXAMPLE 18 except the amounts of the monomer

and the additive. They are listed in the following Table 4.

5

Table 4

| Components | | | | | | | | | | Comp. & Prop. of dope dur. polymeriza. |
|------------|------------------------|----------|--------------|---------|----------------|-----------|---------------------|---------------------|-----------------|--|
| TPC (g) | Comp. of Arom. diamine | | LiCl (g) | | Pyri dine (ml) | DMAC (ml) | Conc. of mon. (wt%) | Conc. of pol. (wt%) | Opt. Prop. Vis. | Int. Pol. |
| | DACYB (Ag) | DAB (Bg) | Mol Rai. A:B | ml DMAC | (g/100 ml) | (ml) | | | | |
| EX. 19 | 5.60 | 3.48 | 3.14 | 50:50 | 1.75 (3.5) | 7.3 | 50 | 18.0 | 15.0 | ANISO 5.3 |
| EX. 20 | 8.26 | 6.16 | 3.70 | 60:40 | 2.28 (3.2) | 10.8 | 74.3 | 18.0 | 15.0 | ANISO 3.8 |
| EX. 21 | 5.55 | 4.14 | 2.49 | 60:40 | 1.5 (3.0) | 7.3 | 50 | 18.0 | 15.0 | ANISO 5.0 |
| EX. 22 | 6.09 | 5.68 | 1.70 | 75:25 | 2 (4) | 7.9 | 50 | 19.2 | 16.1 | ANISO 3.8 |

10

15

20

EXAMPLE 23

Preparation of an aromatic polyamide filament

25 The optical anisotropic aromatic polyamide dope composed of DACYB 75 mol % / DAB 25 mol % of an aromatic diamine monomer which was prepared in EXAMPLE 22 was extrusion-spun into 0.5 to 2 cm of an air layer through nozzle and, at the same time, coagulated in the 20 % by weight of dimethyl acetamide aqueous solution at 30 5°C and then wound into a roller at a maximum speed. After being sufficiently washed with distilled water, the filament was dried in a drier at 150°C. The dried filament had a fineness of 1.2 denier, a tensile strength of 12 g/d, an elongation of 5 % and a tensile 35 modulus of 500 g/d.

EXAMPLE 24

Preparation of an aromatic polyamide filament

5 The optical anisotropic aromatic polyamide dope
composed of DACYB 60 mol % / DAB 40 mol % of an aromatic
diamine monomer which was prepared in EXAMPLE 21 was
extrusion-spun into 0.5 to 2 cm of an air layer
through nozzle and, at the same time, coagulated in the
10 20 % by weight of dimethyl acetamide aqueous solution at
5°C and then wound into a roller at a maximum speed.
After being sufficiently washed with distilled water,
the filament was dried in a drier at 150°C. The dried
filament had a fineness of 1.1 denier, a tensile
15 strength of 21 g/d, an elongation of 5 % and a tensile
modulus of 500 g/d.

EXAMPLE 25

20 Preparation of an optical anisotropic aromatic
polyamide dope

50 ml of dimethylacetamide (DMAc) was charged into
a reactor and dissolved under nitrogen stream, and 1.75
25 g of LiCl was added and dissolved and then 5.97 g of 2-
cyano-1,4-phenylenediamine (CYPPD) was added. After the
solution was completely dissolved, 11.9 ml of pyridine
was added. Then, the solution was cooled down below
20°C using an ice bath and 9.10 g of terephthaloyl
30 chloride (TPC) in a powder form was added with vigorous
stirring. The solution become a viscous polymer
solution with an optical anisotropy at the moment of
adding terephthaloyl chloride. The polymer solution was
slowly stirred for an additional day. The anisotropy of
35 the dope was confirmed by a polarized microscope. The
intrinsic viscosity of th obtained copolymerized

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aromatic polyamide was 3.9.

EXAMPLE 26

5 Preparation of an optical anisotropic aromatic
 polyamide dope

10 50 ml of dimethylacetamide (DMAc) was charged into
 a reactor and dissolved under nitrogen stream, and 2 g
 of LiCl was added and dissolved and then 4.32 g of 2-
 cyano-1,4-phenylenediamine (CYPPD) and 1.50 g of p-
 phenyl diamine were added. After the solution was
 completely dissolved, 12.3 ml of pyridine was added.
15 Then, the solution was cooled down below 20°C using an
 ice bath and 9.40 g of terephthaloyl chloride (TPC) in
 a powder form was added with vigorous stirring. The
 solution become a viscous polymer solution with an
 optical anisotropy at the moment of adding terephthaloyl
 chloride. The polymer solution was slowly stirred for
20 an additional day. The anisotropy of the dope was
 confirmed by a polarized microscope. The intrinsic
 viscosity of the obtained copolymerized aromatic
 polyamide was 2.4.

25

EXAMPLE 27

Preparation of an optical anisotropic aromatic
 polyamide dope

30 50 ml of dimethylacetamide (DMAc) was charged into
 a reactor and dissolved under nitrogen stream, and 2 g
 of LiCl was added and dissolved and then 5.51 g of 4,4'-
 diamino 2-cyano benzanylineimide and 0.97 g of 1,4-
 phenylene diamine (CYPPD) were added. After the
35 solution was completely dissolved, 12.3 ml of pyridine
 was added. Then, the solution was cooled down below

20°C using an ice bath and 5.91 g of terephthaloyl chloride (TPC) in a powder form was added with vigorous stirring. The solution become a viscous polymer solution with an optical anisotropy at the moment of adding terephthaloyl chloride. The polymer solution was slowly stirred for an additional day. The anisotropy of the dope was confirmed by a polarized microscope. The limiting viscosity of the obtained copolymerized aromatic polyamide was 3.1.

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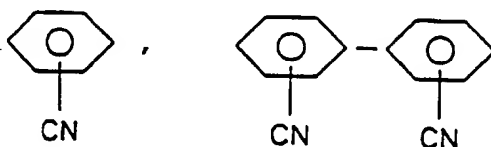
WHAT IS CLAIMED IS:

1. An aromatic polyamide represented by the structural formula (I)

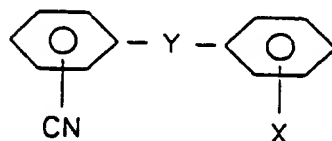
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10 wherein, R represents an aromatic diamine such as



15 or



20 having a nitrile group substituted on the aromatic nucleus of which amount is 25 to 100 mol % of the total aromatic diamine

25 where X represents H, Cl, Br, I, NO₂ or an alkoxy group having 1 to 4 carbon atoms, n represents an integer between 10 and

100,000, y represents $\overset{\text{O}}{\parallel}\text{CNH}$ or $\overset{\text{O}}{\parallel}\text{NEC}$,

and R' represents

30



or

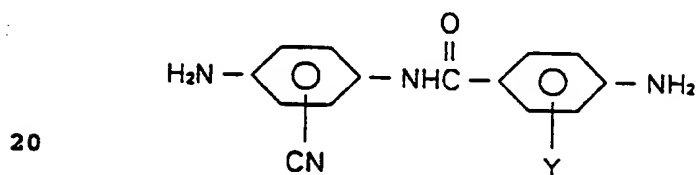
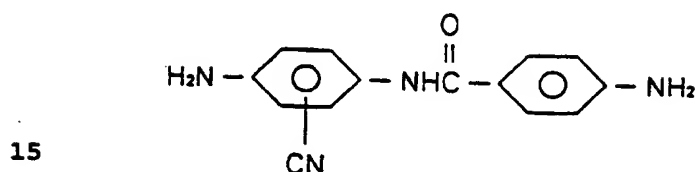
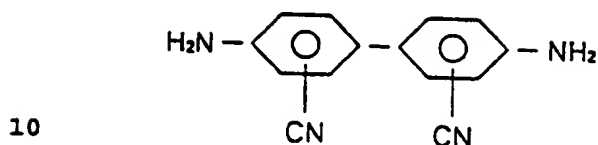
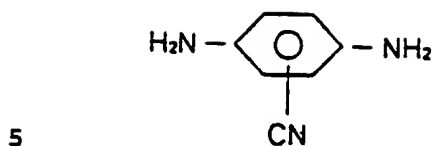


2. An aromatic polyamide represented by the structural
5 formula (I) as claimed in claim 1, characterized in that
the absorption band of a nitrile group is shown at 2230
cm⁻¹ of the infrared spectrum.
3. An aromatic polyamide represented by the structural
10 formula (I) as claimed in claim 1, characterized in that
it is soluble in the polar organic solvent having an
inorganic salt.
4. An aromatic polyamide represented by the structural
15 formula (I) as claimed in claim 1, characterized in that
it has a molecular weight showing 2 to 10 of the
intrinsic viscosity.
5. A process for preparing an optical anisotropic
20 polymer dope of the aromatic polyamide represented by
the structural formula (I) comprising the steps of:
- preparing a solvent for polymerization from an
amide type organic solvent, an urea type organic solvent
25 or a mixture thereof;
- adding 25 to 100 mol % of an aromatic diamine
having a nitrile group substituted on the aromatic
nucleus in the total aromatic diamine in the solvent for
30 polymerization;
- adding pyridine as a polycondensation catalyst in
the obtained solution;
- 35 adding an aromatic diacid halide in the solution

with vigorous stirring at 0 to 50°C; and

continuing the stirring for 1 to 360 minutes.

- 5 6. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the organic solvent is selected from the group consisting of N-methyl-2-pyrrolidone, N,N-dimethyl acetamide, hexamethyl phosphoamide, 10 N,N,N',N'-tetramethyl urea, N,N-dimethyl formamide and dimethyl sulfoxide.
- 15 7. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the inorganic salt is selected from the group consisting of or more of CaCl₂, LiCl, NaCl, KCl, LiBr and KBr.
- 20 8. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5 or 7, characterized in that the added amount of the inorganic salt is lower than 12 % by weight of the total amount of the solvent for polymerization.
- 25 9. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the aromatic diamine having a nitrile group substituted on the aromatic nucleus is selected from the group consisting of
- 30



where Y represents Cl, Br, I, NO₂, or an alkoxy group having 1 to 4 carbon atoms.

25

10. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the aromatic diacid halide is selected from the group consisting of terephthalic chloride, isophthalic chloride, naphthalic chloride, diphenyl chloride or a substituent thereof with Cl, Br, I, NO₂, or an alkyl or alkoxy group having 1 to 4 carbon atoms.

35

11. A process for preparing an optical anisotropic

polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the aromatic diamine not having a nitrile group substituted on the aromatic nucleus is selected from the group consisting of diamino benzanilide, benzidine and phenylene diamine.

12. An optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I), which is prepared by a process defined in any of claims 5 to 11.

13. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) comprising the steps of:

preparing a solvent for polymerization from an amide type organic solvent, an urea type organic solvent or a mixture thereof;

adding 25 to 100 mol % of an aromatic diamine having a nitrile group substituted on the aromatic nucleus in the total aromatic diamine in the solvent for polymerization;

adding the aromatic diacid halide in the solution with vigorous stirring at 0 to 50°C;

keeping the gel type polymer obtained in the above third step for 0 to 24 hours; and

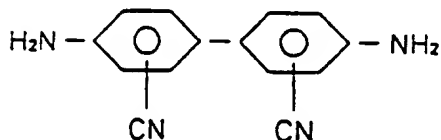
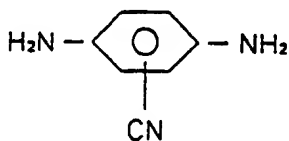
adding and dissolving an inorganic alkali compound.

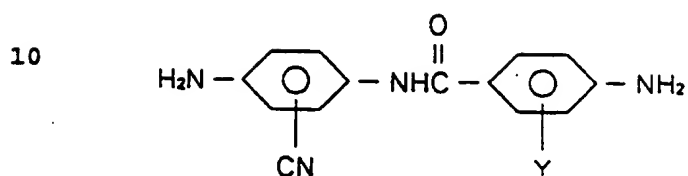
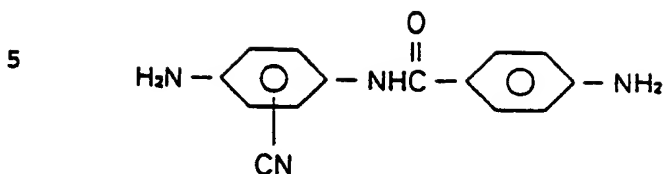
14. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 13,

characterized in that the gel type polymer obtained in the third step is kept for 0 to 24 hours, and an inorganic alkali compound selected from the group consisting of a carbonate, hydride, hydroxide or oxide of an alkali metal and/or an alkali earth metal such as Li_2CO_3 , CaCO_3 , LiH , CaH_2 , LiOH , Ca(OH)_2 , Li_2O or CaO , is added and dissolved with stirring for 1 hour to a few days to obtain a high viscosity polymer solution which shows silver-white brightness during stirring.

15. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 13, characterized in that the added amount of the inorganic alkali compound selected from the group consisting of a carbonate, hydride, hydroxide or an alkali metal and/or an alkali earth metal such as Li_2CO_3 , CaCO_3 , LiH , CaH_2 , LiOH , Ca(OH)_2 , Li_2O or CaO , is 10 to 200 mol % of the required equivalent to neutralize the HCl produced during the polymerization reaction.

16. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 13, characterized in that the aromatic diamine having a nitrile group substituted on the aromatic nucleus is selected from the group consisting of





15

where Y represents Cl, Br, I, NO₂ or an alkoxy group having 1 to 4 carbon atoms.

20 17. An optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I), which is prepared by a process defined any of claims 13 to 16.

25 18. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 13, characterized in that the aromatic diamine not having a nitrile group substituted on the aromatic nucleus is
30 selected from the group consisting of diamino benzanilide, benzidine and phenylene diamine.

35 19. An optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I), which is prepared by a process defined in any of claims 13 to 18.

20. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I), characterized in that the added amount of the aromatic polyamide represented by the structural formula (I) is at least 7 % by weight and dissolved in a polar inorganic solvent having 1 % or more by weight of an inorganic salt at 20 to 100°C.
21. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20, characterized in that the amount of the aromatic polyamide represented by the structural formula (I) is 7 to 23 % by weight in the dope.
22. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20 or 21, characterized in that the aromatic polyamide represented by the structural formula (I) has a molecular weight showing 2 to 10 of limiting viscosity.
23. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20, characterized in that the content of the inorganic salt is 1 to 10 % by weight in the polar organic salt.
24. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20 or 21, characterized in that the inorganic salt is selected from the group consisting one or more of CaCl_2 , LiCl , NaCl , KCl , LiBr and KBr .
25. An optical anisotropic polymer dope of the aromatic

polyamide represented by the structural formula (I), which is prepared by a process defined in any of claims 20 to 24.

5 26. An article produced by the group consisting of polyamide fibers, pulps or films represented by the structural formula (I), which is obtained by spinning and coagulating the optical anisotropic spinning dope of the polyamide represented by said structural formula
10 (I).

27. An article as claimed in claim 26, characterized in that the polyamide fiber represented by the structural formula (I) has a tensile strength of 10 g/d or more and
15 a tensile modulus of 450 g/d or more.

AMENDED CLAIMS

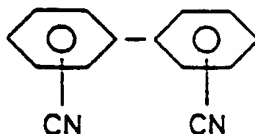
[received by the International Bureau on 17 december 1996 (17.12.96);
original claim 2 cancelled; original claim 1 amended; remaining
claims unchanged (9 pages)]

1. An aromatic polyamide represented by the
structural formula (I)

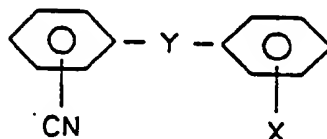
5



10 wherein, R represents an aromatic diamine such as



15 or

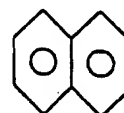


20 having a nitrile group substituted on the aromatic
nucleus of which amount is 25 to 100 mol % of the total
aromatic diamine

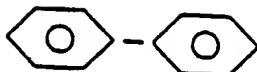
25 where X represents H, Cl, Br, I, NO₂ or an alkoxy group
having 1 to 4 carbon atoms, n represents an integer
between 10 and

100,000, y represents CNH or NHC,
and R' represents

30



or



5 wherein the absorption band of a nitrile group is shown at 2100 to 2400 cm^{-1} of the infrared spectrum.

2. (Canceled)

10 3. An aromatic polyamide represented by the structural formula (I) as claimed in claim 1, characterized in that it is soluble in the polar organic solvent having an inorganic salt.

15 4. An aromatic polyamide represented by the structural formula (I) as claimed in claim 1, characterized in that it has a molecular weight showing 2 to 10 of the intrinsic viscosity.

20 5. A process for preparing an optical isotropic polymer dope of the aromatic polyamide represented by the structural formula (I) comprising the steps of:

25 preparing a solvent for polymerization from an amide type organic solvent, an urea type organic solvent or a mixture thereof;

30 adding 25 to 100 mol % of an aromatic diamine having a nitrile group substituted on the aromatic nucleus in the total aromatic diamine in the solvent for polymerization;

adding pyridine as a polycondensation catalyst in the obtained solution;

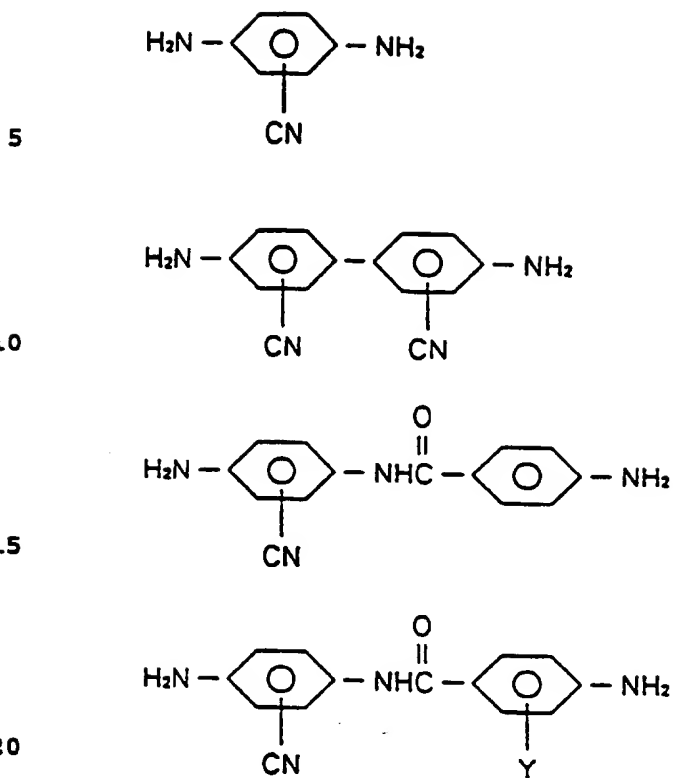
35 adding an aromatic diacid halide in the solution

with vigorous stirring at 0 to 50°C; and

continuing the stirring for 1 to 360 minutes.

- 5 6. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the organic solvent is selected from the group consisting of N-methyl-2-pyrrolidone,
10 N,N-dimethyl acetamide, hexamethyl phosphoamide, N,N,N',N'-tetramethyl urea, N,N-dimethyl formamide and dimethyl sulfoxide.
- 15 7. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the inorganic salt is selected from the group consisting of or more of CaCl₂, LiCl, NaCl, KCl, LiBr and KBr.
- 20 8. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5 or 7, characterized in that the added amount of the inorganic salt is lower than 12 % by weight of the total amount of the solvent for polymerization.
- 25 9. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the aromatic diamine having a nitrile group substituted on the aromatic nucleus is selected from the group consisting of

35



where Y represents Cl, Br, I, NO₂, or an alkoxy group having 1 to 4 carbon atoms.

25

10. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the aromatic diacid halide is selected from the group consisting of terephthalic chloride, isophthalic chloride, naphthalic chloride, diphenyl chloride or a substituent thereof with Cl, Br, I, NO₂, or an alkyl or alkoxy group having 1 to 4 carbon atoms.

35

11. A process for preparing an optical anisotropic

polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 5, characterized in that the aromatic diamine not having a nitrile group substituted on the aromatic nucleus is
5 selected from the group consisting of diamino benzanilide, benzidine and phenylene diamine.

12. An optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I),
10 which is prepared by a process defined in any of claims 5 to 11.

13. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by
15 the structural formula (I) comprising the steps of:

preparing a solvent for polymerization from an amide type organic solvent, an urea type organic solvent or a mixture thereof;

20 adding 25 to 100 mol % of an aromatic diamine having a nitrile group substituted on the aromatic nucleus in the total aromatic diamine in the solvent for polymerization;

25 adding the aromatic diacid halide in the solution with vigorous stirring at 0 to 50°C;

30 keeping the gel type polymer obtained in the above third step for 0 to 24 hours; and

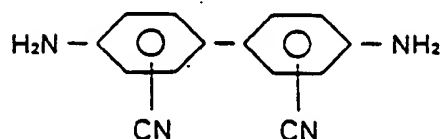
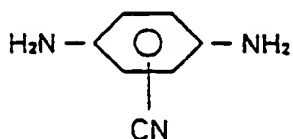
adding and dissolving an inorganic alkali compound.

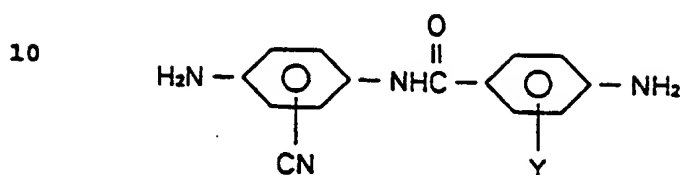
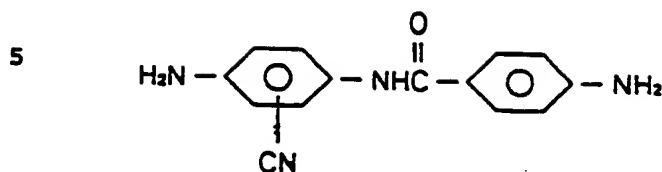
14. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by
35 the structural formula (I) as claimed in claim 13,

characterized in that the gel type polymer obtained in the third step is kept for 0 to 24 hours, and an inorganic alkali compound selected from the group consisting of a carbonate, hydride, hydroxide or oxide of an alkali metal and/or an alkali earth metal such as Li_2CO_3 , CaCO_3 , LiH , CaH_2 , LiOH , Ca(OH)_2 , Li_2O or CaO , is added and dissolved with stirring for 1 hour to a few days to obtain a high viscosity polymer solution which shows silver-white brightness during stirring.

15. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 13, characterized in that the added amount of the inorganic alkali compound selected from the group consisting of a carbonate, hydride, hydroxide or an alkali metal and/or an alkali earth metal such as Li_2CO_3 , CaCO_3 , LiH , CaH_2 , LiOH , Ca(OH)_2 , Li_2O or CaO , is 10 to 200 mol % of the required equivalent to neutralize the HCl produced during the polymerization reaction.

16. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 13, characterized in that the aromatic diamine having a nitrile group substituted on the aromatic nucleus is selected from the group consisting of





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where Y represents Cl, Br, I, NO₂ or an alkoxy group having 1 to 4 carbon atoms.

20 17. An optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I), which is prepared by a process defined any of claims 13 to 16.

25 18. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 13, characterized in that the aromatic diamine not having a nitrile group substituted on the aromatic nucleus is selected from the group consisting of diamino
30 benzanilide, benzidine and phenylene diamine.

35 19. An optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I), which is prepared by a process defined in any of claims 13 to 18.

20. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I), characterized in that the added amount of the aromatic polyamide represented by the structural formula (I) is at least 7 % by weight and dissolved in a polar inorganic solvent having 1 % or more by weight of an inorganic salt at 20 to 100°C.

21. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20, characterized in that the amount of the aromatic polyamide represented by the structural formula (I) is 7 to 23 % by weight in the dope.

22. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20 or 21, characterized in that the aromatic polyamide represented by the structural formula (I) has a molecular weight showing 2 to 10 of limiting viscosity.

23. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20, characterized in that the content of the inorganic salt is 1 to 10 % by weight in the polar organic salt.

24. A process for preparing an optical anisotropic polymer dope of the aromatic polyamide represented by the structural formula (I) as claimed in claim 20 or 21, characterized in that the inorganic salt is selected from the group consisting one or more of CaCl₂, LiCl, NaCl, KCl, LiBr and KBr.

25. An optical anisotropic polymer dope of the aromatic

polyamide represented by the structural formula (I), which is prepared by a process defined in any of claims 20 to 24.

5 26. An article produced by the group consisting of polyamide fibers, pulps or films represented by the structural formula (I), which is obtained by spinning and coagulating the optical anisotropic spinning dope of the polyamide represented by said structural formula
10 (I).

27. An article as claimed in claim 26, characterized in that the polyamide fiber represented by the structural formula (I) has a tensile strength of 10 g/d or more and
15 a tensile modulus of 450 g/d or more.

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FIG.1

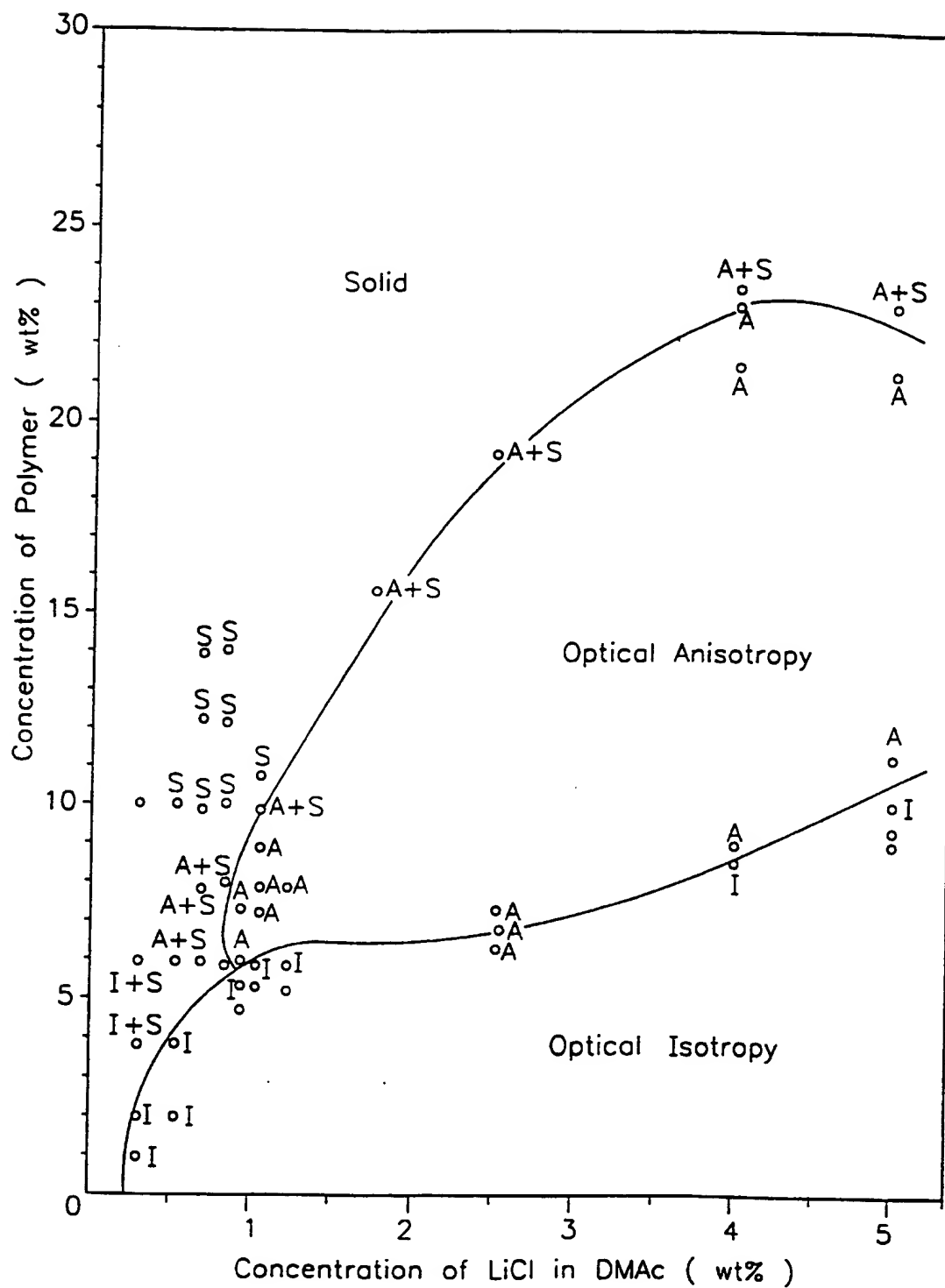
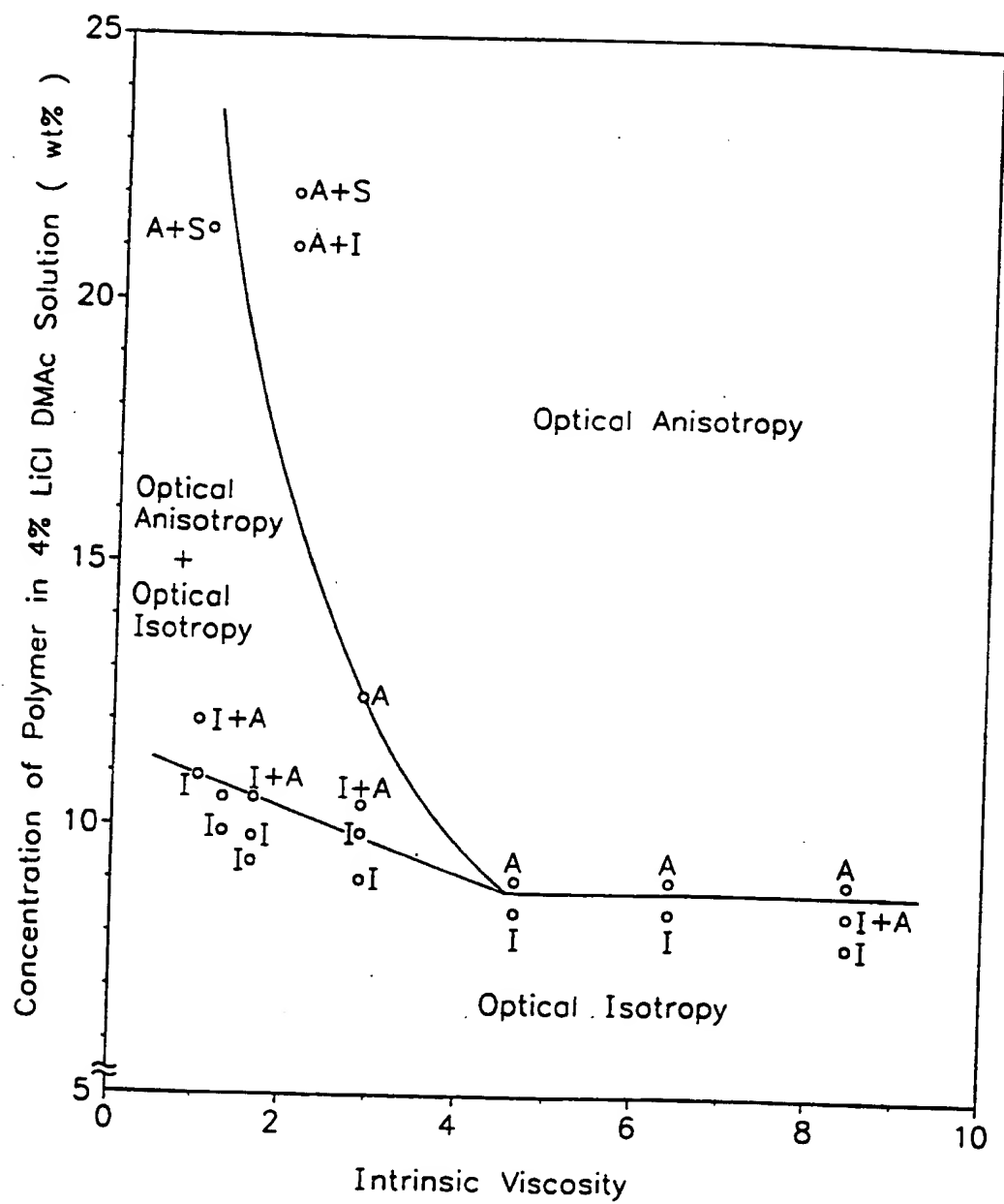
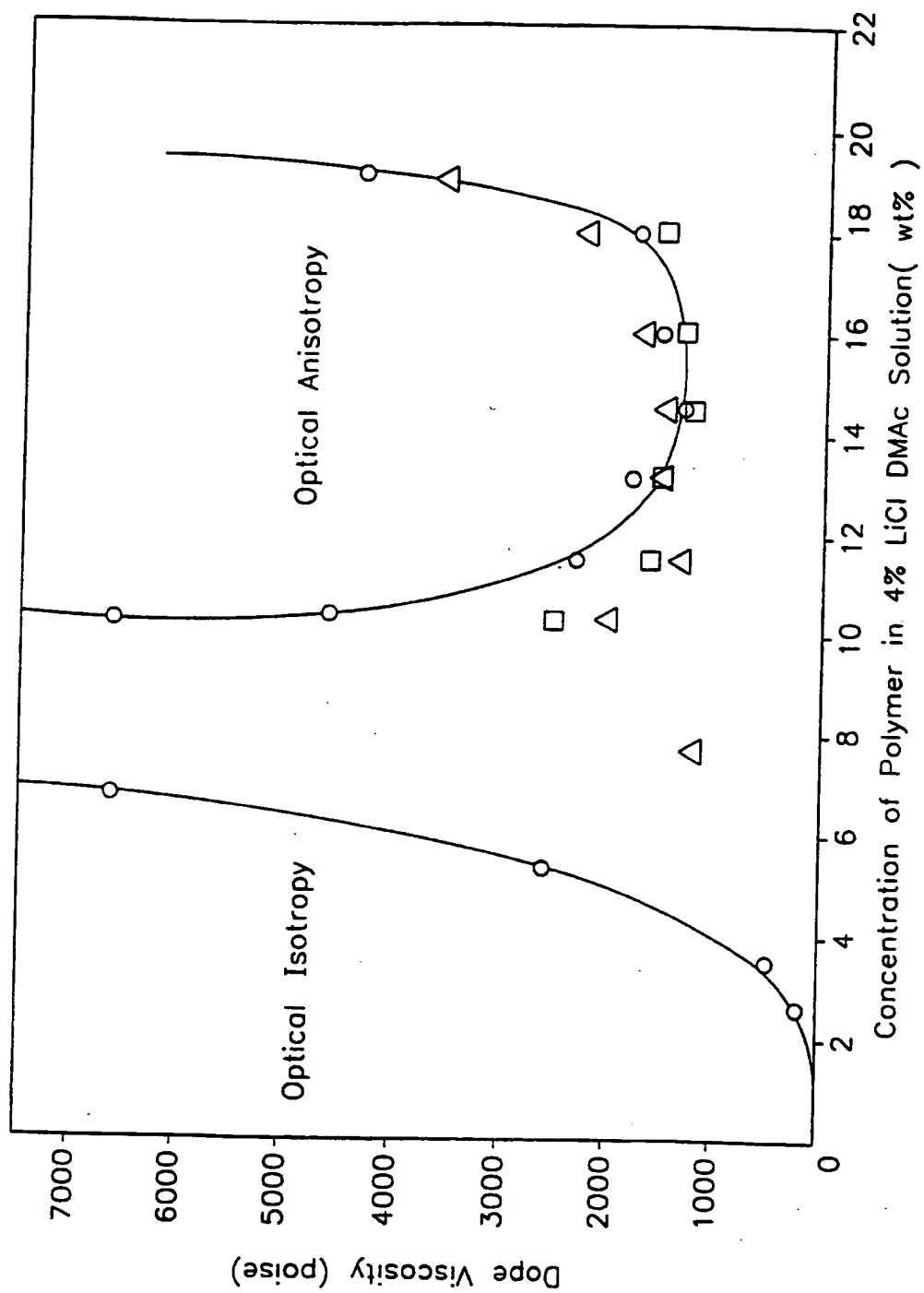


FIG.2



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FIG.3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 96/00107

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 08 G 69/32; D 01 F 6/60; C 08 J 5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 08 G 69/32; D 01 F 6/60; C 08 J 5/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, PAJ, WPIL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|------------------------|
| X | EP 0 045 934 A1 (TEIJIN LIMITED) 17 February 1982 (17.02.82), claims; page 5, lines 11-25; page 7, lines 1-5; page 8, line 13 - page 9, line 23; example 1. | 1,3-27 |
| X | US 4 021 415 A (CHANG) 03 May 1977 (03.05.77), claims; example 4; column 2, line 49 - column 3, line 63. | 1,3,5,6,9, 11,12,26 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search

07 October 1996 (07.10.96)

Date of mailing of the international search report

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Name and mailing address of the ISA/AT

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR 96/00107

| In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche | Datum der Veröffentlichung Publication date Date de publication | Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets | Datum der Veröffentlichung Publication date Date de publication |
|--|--|--|--|
| EP A1 45934 | 17-02-82 | DE C0 3167607 EP B1 45934 JP A2 57034125 JP B4 1034254 US A 4507467 | 17-01-85 05-12-84 24-02-82 18-07-82 26-03-83 |
| US A 4021415 | 03-05-77 | keine - none - rien | |